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MASTER

OPTICAL STUDIES OF CADMIUM

Ph. D. Thesis Submitted to Iowa State University, August 1970

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OPTICAL STUDIES OF CADMIUM

by

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August 1970

OPTICAL STUDIES OF CADMIUM

Roger James Bartlett

ABSTRACT

The reflectivity and/or absorptivity of cadmium was measured from 0.15 eV to 20 eV. Measurements were made using polarized light with the electric vector of the incident radiation both perpendicular and parallel to the c-axis of the crystal.

In the visible and infrared spectra both polarization cases had strong absorption peaks. In the perpendicular polarization case the main peak was at 0.98 eV and was attributed mainly to transitions between bands two and three along the LH symmetry line. Also in this polarization there was an absorption edge at 0.29 eV. This may be due to transitions near the point K in the Brillouin zone. For the parallel polarization case the main absorption peak was at 1.10 eV. The absorption here was attributed to transitions between bands two and three along Γ K, Γ M and LH. No low energy absorption edge was found for the parallel polarization case. Agreement between the experimental data and the theoretical calculations based on a nonlocal pseudopotential model was good. However, there was no agreement between the data and calculations based on a local pseudopotential model.

At low temperatures, the long wavelength absorptivities were

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approximately constant. This agrees with the theories of Kliewer and Fuchs and of Holstein for the anomalous skin effect region. Using the theory of Kliewer and Fuchs and the experimental data, parallel and perpendicular effective masses were calculated. The values were 1.09 m and 1.61 m, respectively. The weighted average of $m_{||}^*$ and $m_{\perp}^*$ is in good agreement with the thermal effective mass for cadmium. The low energy data support the theory of Kliewer and Fuchs and tend to confirm the volume absorption process suggested by Holstein.

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INTRODUCTION

Preliminary Remarks

The use of optical methods to investigate the properties of solids has proven to be very valuable. Such phenomena as color centers, excitons, interband transitions, collective effects and other phenomena of matter have been examined by optical means. Here the reflectivity and/or absorptivity of cadmium, a hexagonal crystal, have been measured in the wavelength range from $7\text{ }\mu\text{m}$ to $600\text{ }\text{\AA}$. The measurements were made using polarized light. In one case the polarization vector of the light was parallel to the c-axis of the crystal and in the other case it was perpendicular. A lack of optical data for cadmium in the literature as well as the possibility of interesting anisotropic effects prompted this study.

In the following section a review of optical constants is given. These optical constants are the "go between" in relating the experimental data to the electronic behavior of the material. Excellent references pertaining to the subsequent discussion are Stern (1) and Givens (2).

Optical Constants

The interaction of a light beam with a metal can be described in terms of Maxwell's equations and the optical constants of the metal. In Gaussian units for a nonmagnetic material, Maxwell's equations are:

$$\vec{\nabla} \cdot \vec{D} = 4\pi\rho \quad (1)$$

$$\vec{\nabla} \cdot \vec{B} = 0 \quad (2)$$

$$\nabla \times \bar{E} + \frac{1}{c} \frac{\partial \bar{B}}{\partial t} = 0 \quad (3)$$

$$\nabla \times \bar{B} = \frac{4\pi}{c} \bar{J} + \frac{1}{c} \frac{\partial \bar{D}}{\partial t} \quad (4)$$

where $\bar{D}$ is the displacement, ρ is the charge density, $\bar{B}$ is the magnetic flux density, $\bar{E}$ is the electric field, and $\bar{J}$ is the current density.

In Equation 4 it is convenient to set

$$4\pi\bar{J} + \frac{\partial \bar{D}}{\partial t} = \frac{\partial \bar{D}'}{\partial t} \quad (5)$$

where $\bar{D}'$ is a generalized displacement. The generalized displacement is related to the total (displacement plus real) current by

$$4\pi\bar{J}_t = \frac{\partial \bar{D}'}{\partial t} \quad (6)$$

When this is done Equations 3 and 4 can be combined to give a wave equation i.e.,

$$\nabla^2 \bar{E} - \frac{1}{c^2} \frac{\partial^2 \bar{D}'}{\partial t^2} = \nabla(\nabla \cdot \bar{E}) \quad (7)$$

To proceed from here it is necessary to relate the generalized displacement vector, $\bar{D}'$, to the electric field, $\bar{E}$. If it is assumed that the effect of the electric field is to cause the displacement and that the relation between them is linear and time-independent, then a convolution integral can be used to relate $\bar{E}$ and $\bar{D}'$, i.e.,

$$D_i(\bar{x}, t) = \int \tilde{\epsilon}_{ig}(\bar{x} - \bar{x}', t - t') E_g(\bar{x}', t') d^3x' dt' \quad (8)$$

where the Einstein summation convention has been used and $\tilde{\epsilon}_{ig}$ is the complex dielectric function, a second rank tensor. If it is assumed

temporarily that the dielectric function can be expressed as a local function, i.e.,

$$\tilde{\epsilon}(\bar{x} - \bar{x}', t - t') = \tilde{\epsilon}(\bar{x} - \bar{x}', t - t') \delta(\bar{x} - \bar{x}') \quad (9)$$

where $\delta(\bar{x} - \bar{x}')$ is the Dirac delta function, then the generalized displacement can be written as

$$D_i^1(\bar{x}, t) = \int \tilde{\epsilon}_{ig}(\bar{x}, t - t') E_g^1(\bar{x}, t') dt' \quad (10)$$

The Fourier transform of the time component of this equation can be taken with the result that

$$D_i^1(\bar{x}, \omega) = \tilde{\epsilon}_{ig}(\omega) E_g^1(\bar{x}, \omega) \quad (11)$$

If Equation 11 is substituted into the wave equation the result is

$$\frac{\partial^2}{\partial x_g \partial x_g} E_i + \frac{\omega^2}{c^2} \tilde{\epsilon}_{ig} E_g = \frac{\partial}{\partial x_i} \frac{\partial E_g}{\partial x_g} \quad (12)$$

For convenience in discussing Equation 12 as it applies to a uniaxial material, the geometry shown in Figure 1 will be used. It should be noted that the c-axis (optic-axis) of the crystal is in the plane of the surface and lies along the y-coordinate axis. Because of the symmetry properties of the uniaxial crystal the tensor dielectric constant has only two independent components. In the coordinate system used here the tensor components form a diagonal matrix that can be written as

$$\tilde{\epsilon} = \begin{pmatrix} \tilde{\epsilon}_{xx} & 0 & 0 \\ 0 & \tilde{\epsilon}_{yy} & 0 \\ 0 & 0 & \tilde{\epsilon}_{zz} \end{pmatrix} \quad (13)$$

where

$$\tilde{\epsilon}_{xx} = \tilde{\epsilon}_{zz} \equiv \tilde{\epsilon}_\perp \quad (14)$$

Figure 1. Orientation of the sample showing the electric field of the incident wave for P-polarization, E_p , and for S-polarization, E_s

and
$$\tilde{\epsilon}_{yy} \equiv \tilde{\epsilon}_{\parallel} \quad (15)$$

The parallel, $\parallel$, and perpendicular, $\perp$, symbols refer to the directions parallel and perpendicular to the c-axis of the crystal, respectively.

If polarized light is incident on the sample as shown in Figure 1, further simplification results. Now the tensor product $\epsilon_{ig} E_g$ can be written as $\tilde{\epsilon}_{\perp} \bar{E}_p$ for P-polarized light and as $\tilde{\epsilon}_{\parallel} \bar{E}_s$ for S-polarized light. The designation P-polarization is applied to light that has its electric vector in the plane of reflection and S-polarization, to light that has its electric vector perpendicular to the plane of reflection. Equation 12 can now be written for the two polarization cases in the following way:

$$\nabla^2 \bar{E}_p + \frac{\omega^2}{c^2} \tilde{\epsilon}_{\perp} \bar{E}_p = 0 \quad (16)$$

for the P-polarization case and

$$\nabla^2 \bar{E}_s + \frac{\omega^2}{c^2} \tilde{\epsilon}_{\parallel} \bar{E}_s = 0 \quad (17)$$

for the S-polarization case. Plane wave solutions to Equations 16 and 17 are

$$\bar{E}_p = \bar{E}_{po} e^{i(\bar{k}_p \cdot \bar{x} - \omega t)} \quad (18)$$

where

$$k_p^2 = \frac{\omega^2}{c^2} \tilde{\epsilon}_{\perp} = \frac{\omega^2}{c^2} (\epsilon_{1\perp} + i\epsilon_{2\perp}) \quad (19)$$

and

$$\bar{E}_s = \bar{E}_{so} e^{i(\bar{k}_s \cdot \bar{x} - \omega t)} \quad (20)$$

where

$$k_s^2 = \frac{\omega^2}{c^2} \tilde{\epsilon}_{11} = \frac{\omega^2}{c^2} (\epsilon_{11} + i\epsilon_{21}) \quad (21)$$

The term involving the divergence of $\bar{E}$ on the right hand side of Equation 12 does not contribute since there are no free charges in a conductor. This is evident from the following equations. If there are no free charges, then

$$\bar{\nabla} \cdot \bar{D} = 0 \quad (22)$$

or

$$\frac{\partial}{\partial x_i} \epsilon_{ig} E_g = 0 \quad (23)$$

which can be written as

$$\epsilon_{\perp} \frac{\partial}{\partial x_{\perp}} \bar{E}_p + \epsilon_{11} \frac{\partial}{\partial x_{11}} \bar{E}_s = 0 \quad (24)$$

Thus it can be seen that for either polarization the term involving $\text{div } \bar{E}$ is zero. It should be noted that had unpolarized light been used here, or had the direction of polarization with respect to the crystal axis been different, this separation of ϵ_{11} and $\epsilon_{\perp}$ would not have been possible.

By using Equation 5 and the constitutive equations

$$\bar{J}_{11} = \sigma_{11} \bar{E}_{11}, \quad (25)$$

$$\bar{J}_{\perp} = \sigma_{\perp} \bar{E}_{\perp}, \quad (26)$$

and

$$\bar{D}_{11} = \epsilon_{11} \bar{E}_{11}, \quad (27)$$

$$\bar{D}_{\perp} = \epsilon_{\perp} \bar{E}_{\perp}, \quad (28)$$

relations between the generalized dielectric constant and the usual Maxwell permittivity, ϵ , and conductivity, σ , can be found. The relations are:

$$\tilde{\epsilon}_{||} = \epsilon_{||} + i \frac{4\pi\sigma_{||}}{\omega} \quad (29)$$

and

$$\tilde{\epsilon}_{\perp} = \epsilon_{\perp} + i \frac{4\pi\sigma_{\perp}}{\omega} . \quad (30)$$

To relate the generalized dielectric constant to the reflectivity of the crystal the two polarization cases are considered separately. The boundary conditions at the air-metal interface required by Maxwell's equations, establish a relationship between the incident electric field and the reflected electric field. From this relation the reflectivity is found. The boundary conditions are 1) the tangential components of $\vec{B}$ and $\vec{E}$ are continuous and 2) the normal components of $\vec{B}$ and $\vec{D}$ are continuous. Using these boundary conditions and Equations 1 through 4, the reflectivity for the P-polarization case is found to be

$$R_p = \left| \frac{\tilde{\epsilon}_{\perp} \cos \varphi - \sqrt{\tilde{\epsilon}_{\perp} - \sin^2 \varphi}}{\tilde{\epsilon}_{\perp} \cos \varphi + \sqrt{\tilde{\epsilon}_{\perp} - \sin^2 \varphi}} \right|^2 \quad (31)$$

and for the S-polarization case

$$R_s = \left| \frac{\frac{\sqrt{\tilde{\epsilon}_{||} - \sin^2 \varphi}}{\sqrt{\tilde{\epsilon}_{||} - \sin^2 \varphi}} - \cos \varphi}{\frac{\sqrt{\tilde{\epsilon}_{||} - \sin^2 \varphi}}{\sqrt{\tilde{\epsilon}_{||} - \sin^2 \varphi}} + \cos \varphi} \right|^2 \quad (32)$$

where φ is the angle of incidence.

The Poynting vector, $\vec{S}$, can be derived from Equations 3 and 4. It is the flux of energy in an electromagnetic wave and is given by

$$\bar{S} = \frac{c}{4\pi} \bar{E} \times \bar{B} . \quad (33)$$

From the Poynting vector the energy loss per unit volume per unit time can be found. It is

$$-\nabla \cdot \langle \bar{S} \rangle_{\text{time avg}} = \frac{\omega}{8\pi} \epsilon_2 |E_0|^2 \quad (34)$$

where it has been assumed that the fields consist of plane waves with a time dependence of $e^{-i\omega t}$. It is interesting to note that this power loss is proportional to ϵ_2 .

In order to extract information about a material from reflectivity data, it is necessary to relate the generalized dielectric constant to the elementary properties of the material. The generalized dielectric constant is a response function for the system relating the cause, electromagnetic radiation or other perturbation, to the effect, elementary excitations in the material. For the case of optical frequency radiation incident on a metal, elementary excitations that can occur are: 1) collective excitations and 2) single particle excitations within one band or between bands. To calculate $\tilde{\epsilon}$ it is necessary to know the electron wave functions in the material. For this reason it is usually difficult to make exact calculations of $\tilde{\epsilon}$. Approximations are almost always needed. One method used to calculate $\tilde{\epsilon}$ is the self-consistent field method (3). The result of such a calculation is expressed in the following equation

$$\tilde{\epsilon}(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau_c)} - \frac{e^2}{\pi^2 m} \int d^3k \sum_{\ell\ell'} \frac{f_{\ell'}(\bar{k}) f_{\ell}^{\mu}}{[(\omega + \frac{i}{\tau_{\ell\ell'}})^2 - \omega_{\ell\ell'}^2]} \quad (35)$$

where $f_{\ell'}(\bar{k})$ is the Fermi-Dirac distribution function,

$$\omega_{\ell\ell'} = [E_{\ell}(\bar{k}) - E_{\ell'}(\bar{k})] / \hbar, \quad (36)$$

$E_{\ell}(\bar{k})$ is the energy of an electron in band ℓ with wave vector $\bar{k}$, and f_{ℓ}^{μ} is the oscillator strength defined by

$$f_{\ell\ell'}^{\mu} = \frac{2}{\hbar\omega_{\ell\ell'}} |\langle \ell\bar{k} | p^{\mu} | \ell'\bar{k} \rangle|^2. \quad (37)$$

The wave functions in the above matrix element are the spatially periodic part of Bloch functions in states $\bar{k}$ and band ℓ and ℓ' . The momentum component, p^{μ} , is in the direction of the polarization of the incident radiation. It should be noted that the translational invariance of the Bloch functions requires the matrix element to be zero unless

$$\bar{k} - \bar{k}' + \bar{q} = 0. \quad (38)$$

Here the magnitude of the incident light wave vector, $|\bar{q}|$, is negligible, so

$$\bar{k} = \bar{k}'. \quad (39)$$

This is the selection rule for direct optical absorption. The conduction band plasma frequency, ω_p , is defined by

$$\omega_p^2 = \frac{4\pi n e^2}{m^*} \quad (40)$$

where n is the conduction electron density, and $\frac{1}{m^*}$ is the average inverse effective mass of the conduction electrons defined by

$$\frac{1}{m^*} = \frac{1}{4\pi^3 m \hbar^2} \int d^3k \frac{\nabla_k^2 E_c(k)}{3} \quad (41)$$

$E_c(\bar{k})$ is the energy of an electron of wave vector, $\bar{k}$, in the conduction band. In the relaxation time, τ_c , the effects of the imperfect lattice on the conduction electrons are incorporated, while τ_{ul} was introduced phenomenologically to account for broadening effects in interband transitions, which are due to finite lifetimes of the electrons and holes.

Equation 35 is an approximation because a one-particle and not a many-particle hamiltonian was used. The result is equivalent to that of the random phase approximation (4). Also the equation is valid only for the case where the wavelength of the incident radiation is large compared to the interatomic spacing. For optical frequencies this restriction is fulfilled. The first two terms in Equation 35 are the Drude or intraband dielectric constant. Drude (5) first calculated these terms in 1900. Since that time quantum mechanical calculations have been performed showing good agreement with the Drude theory for long wavelength radiation, the corrections to the Drude theory being of the order of $\hbar\omega/E_F$ (6,7) where E_F is the Fermi energy. The last term in the expression for $\tilde{\epsilon}(\omega)$ is the contribution due to interband transitions which occur at certain high photon energies. It is often referred to as $\delta\epsilon^b$. When they exist, the interband effects usually dominate the free electron effects even though both are present.

As shown previously it is the imaginary part of $\tilde{\epsilon}$ that measures the dissipation. When the absorption is due to interband effects, it can be correlated with the band structure of the solid. By writing

$\delta\epsilon^b$ in the following way it is easier to see this correlation. First $\delta\epsilon^b$ is separated into its real and imaginary parts

$$\delta\epsilon^b = \frac{-e^2}{\pi^2 m} P \int d^3k \sum_{\ell\ell'} \frac{f_{\ell'}(\bar{k}) f_{\ell\ell'}^{\mu}}{(\omega^2 - \omega_{\ell\ell'}^2)} + \frac{ie^2}{2\pi m\omega} \int d^3k \sum_{\ell\ell'} f_{\ell'}(\bar{k}) f_{\ell\ell'}^{\mu} \delta(\omega_{\ell\ell'} - \omega). \quad (42)$$

Here ℓ is the filled band, ℓ' , the empty and the relation

$$\lim_{s \rightarrow 0} \frac{1}{x + is} = P \frac{1}{x} - i\pi\delta(x) \quad (43)$$

has been used and $\tau_{\ell\ell'}$ is now infinite. The second term in equation 42 is $\delta\epsilon_2^b$. Recall that $\omega_{\ell\ell'}$ is the difference in energy between an electron in band ℓ and one in band ℓ' both with wave vector $\bar{k}$. Because of the delta-function no contribution to $\delta\epsilon_2^b$ can occur until $\omega = \omega_{\ell\ell'}$. Thus the absorption band edge will occur at the smallest value of $\omega_{\ell\ell'}$. The delta-function implies that the absorption will be a series of spikes. This is not actually true. Broadening of the absorption occurs because there is a finite relaxation time, $\tau_{\ell\ell'}$, not infinite as assumed here. Also, the difference between energy bands is not a constant energy. Next $\delta\epsilon_2^b$ is written in the following way (8):

$$\delta\epsilon_2^b = \frac{e^2 4\pi^2}{m\omega} \sum_{\ell\ell'} f_{\ell\ell'} G_{\ell\ell'} \quad (44)$$

where it is implicitly assumed that the solid is at temperature, $T = 0$ so that all states below the Fermi level are filled and all those above are empty. The function $G_{\ell\ell'}$ is the joint density of states, which can

be written as (8)

$$G_{\ell\ell'} = \frac{1}{8\pi^3} \int \frac{dS}{|\nabla_k (E_\ell - E_{\ell'})|} \quad (45)$$

The integrand is evaluated over the surface given by

$$E_{\ell'}(\bar{k}) - E_\ell(\bar{k}) = \hbar\omega \quad (46)$$

Structure in $\delta\epsilon_2^b$ is due to the joint density of states, $G_{\ell\ell'}$, and to the matrix element $f_{\ell\ell'}$. There is reason to believe that $f_{\ell\ell'}$ is a slowly varying function of $\bar{k}$ and that most of the structure in $\delta\epsilon_2^b$ is due to variations in the joint density of states. However, there is evidence showing that this is not the case for the noble metals, reported by Mueller and Phillips (9). Also, the matrix element, $f_{\ell\ell'}$, is polarization-dependent and so can produce polarization effects in $\delta\epsilon_2^b$. In situations where $f_{\ell\ell'}$ is slowly varying, most of the structure in $\delta\epsilon_2^b$ comes from $G_{\ell\ell'}$. The joint density of states will have large variations near critical points defined in the following way:

$$\bar{\nabla}_k E_\ell(\bar{k}) = \bar{\nabla}_k E_{\ell'}(\bar{k}) = 0 \quad (47)$$

and

$$\bar{\nabla}_k E_\ell(\bar{k}) - \bar{\nabla}_k E_{\ell'}(\bar{k}) = 0 \quad (48)$$

Critical points expressed by Equation 47 occur only at points of high symmetry in the Brillouin zone and are called symmetry interband points. Critical points satisfying Equation 48 are called general interband points and can occur anywhere in the Brillouin zone. General interband points occur when parallel bands exist at the same wave

vector $\bar{k}$. From the above discussion about the joint density of states it seems reasonable to try to relate structure in $\delta\epsilon_2^b$ to energy gaps in the band structure at certain symmetry points.

The above discussion assumes that direct transitions are the dominating mechanism of absorption. However, there are occasions when indirect transitions must be considered. Whenever perturbations other than the electromagnetic field are present, (e.g. impurity scattering or electron-phonon interactions) indirect transitions can occur. The indirect transitions are usually important only when direct transitions are forbidden because of symmetry or at points where direct transitions are not permitted. Photoemission results (10,11) have indicated that nondirect transitions may be important for optical transitions involving filled d-states in transition metals. This is due to a localization of the electron or hole state for a time long compared to the excitation time. There is increasing evidence that indirect transitions may occur when the electromagnetic radiation has a field component perpendicular to the sample surface. It is believed (12) that the surface charge caused by the normal component of the electric field produces longitudinal electric fields in the solid which supply the needed momentum for indirect transitions. At the present time there seems to be a certain amount of uncertainty involved with the indirect processes. Because of this, and the fact that the data can be reasonably explained without them they will be ignored.

Nonlocal, Free Electron Contributions to the Absorptivity

Most of what has been said in the previous section applies only when a local relation exists between the electric field and the generalized displacement vector. That is to say the electric field has been assumed to be spatially uniform over the distance traversed by an electron between collisions. As pointed out by Pippard (13) this cannot be generally valid. It should, however, be a reasonable assumption when the wavelength of the electric field in the material is long compared to the mean free path of the electrons. This is the case for relatively low frequency radiation and is also valid for all frequencies when the temperature of the metal is sufficiently high. A second region where a local relation between $\bar{D}$ and $\bar{E}$ exists is at sufficiently high frequencies where the distance an electron travels during one cycle of the electric field is short compared to the wavelength of the electric field. When neither of these conditions are satisfied the spatial dependence of the electric field must be taken into account. This region is known as the anomalous skin effect region. In this region a nonlocal relation between the electric field and the generalized displacement is required. Through the use of Maxwell's equations and the Boltzmann equation an integrodifferential equation can be derived from which the electric field can be obtained. Reuter and Sondheimer (14) have presented a theory, taking into account the nonlocality of the electric field for the anomalous skin effect. They considered the cases of thick crystals with light incident normally to the surface and both diffuse and specular internal reflection of the electrons. Since this pioneering work the

theory has been expanded to include arbitrary angles on incidence (15, 16, 17) and/or finite thickness samples (18, 19, 20). A recent study of the optical properties of metals considering nonlocal effects has been given by K.L. Kliewer and Ronald Fuchs (21). One of their results is the absorptivity of a thick metal crystal in the infrared region of the spectrum. They find that the absorptivity is given by

$$A = 2\gamma \cos \varphi \left[1 - \frac{1}{8} \left(\frac{v}{\Omega} \right)^2 + \frac{1}{2} \Omega^2 \cos^2 \varphi - \gamma \cos \varphi \right] \quad (49)$$

$$+ \frac{3}{4} \left(\frac{v}{c} \right) \cos \varphi \left[1 - \left(\frac{v}{\Omega} \right)^2 - 2\gamma \cos \varphi \right] + \left(\frac{v}{c} \right)^3 \cos \varphi \left[-\frac{65}{128} \frac{\gamma}{\Omega^2} - \frac{9}{32} \cos \varphi \right]$$

where φ is the angle of incidence, v is the Fermi velocity and c is the velocity of light. γ is a measure of the damping effects in the metal and can be written as

$$\gamma = \frac{1}{\omega_p \tau} \quad (50)$$

where τ is a relaxation time and ω_p is the free carrier plasma frequency. Ω is the dimensionless frequency given by

$$\Omega = \frac{\omega}{\omega_p} \quad (51)$$

This relation should be compared to one derived earlier by Holstein (22). Holstein's relation for diffuse scattering and normal incidence is

$$A = 2\gamma + \frac{3}{4} \frac{v}{c} \quad (52)$$

From a quantum mechanical point of view a conduction electron can absorb a photon only if the electron undergoes scattering which permits conservation of energy and momentum. This being the case, one might

expect that the absorption would decrease rather drastically as the temperature of a sample is lowered since the likelihood of the electrons being scattered in the penetration region of the field should be much smaller. However, experimentally this is not the case (23,24). One finds that the absorption decreases only slightly as the temperature is lowered. One of the reasons for this relatively high absorptivity is that the electrons are diffusely scattered from the surface of the sample, thereby exchanging momentum with the crystal. It is this surface scattering that gives rise to the $\frac{3}{4} \frac{v}{c}$ term in Equation 52 (25). A second scattering mechanism available to the electrons was investigated by Holstein (26). In this case a photon is absorbed by an electron and energy and momentum are conserved by a simultaneous electron-phonon interaction. This process gives rise to an absorptivity of (26)

$$A = \left(\frac{m^*}{4\pi n e^2} \right)^{1/2} \left(\frac{4}{5} \right) \frac{\theta}{T\tau} \quad (53)$$

where θ is the Debye temperature and T is the thermodynamic temperature where τ , the electronic relaxation time, was determined. τ is defined through the dc conductivity at a temperature large compared to θ .

As can be seen this term has the form of

$$\gamma_{\text{eff}} = \frac{1}{\omega_p \tau_{\text{eff}}} \quad (54)$$

where

$$\omega_p^2 = \frac{4\pi n e^2}{m^*} \quad (55)$$

and

$$\tau_{\text{eff}} = \frac{5}{2} \frac{T}{\theta} \tau \quad (56)$$

Thus the volume interaction contributes an additional term to Equation 52 which can be expressed as $2\gamma_{\text{eff}}$. Further experimental evidence that such interactions do take place and are important in the absorption process is given by R.R. Joyce and P.L. Richards (27). They have measured the absorptivity of lead at low temperatures and find that the absorption exhibits vibrational satellites, known as vibronic structure. This is very striking proof of the role of phonons in the absorption process.

The total absorption due to both the surface and the volume terms is just the sum of these two effects; i.e.,

$$A = \frac{m^*}{4\pi n e^2} \left(\frac{4}{5}\right) \frac{\theta}{T\tau} + \frac{3}{4} \frac{v}{c} + 2\gamma \quad . \quad (57)$$

In general it should be the scattering amplitudes that are added and not the absorptivities. The absorptivity is proportional to the square of the scattering amplitude. The cross-product of the amplitudes is neglected, when absorptivities are added. Neglecting this interference term between the surface scattering and volume scattering is generally accepted.

EXPERIMENTAL METHOD

Preliminary Remarks

In making optical measurements, there are essentially three basic quantities that can be measured, the reflectivity, R , the absorptivity, A , and the transmission, T . The sum of these three quantities must be one, i.e.,

$$R + A + T = 1 . \quad (58)$$

These quantities are defined in the following way. The reflectivity is the ratio of the intensity of radiation reflected from the sample to the intensity of the radiation incident on the sample. The intensity has units of energy per unit area per unit time or power per unit area. The reflectivity can be written as

$$R = \frac{P_r}{P_o} \quad (59)$$

where P_r is the power reflected from the sample and P_o is the power incident on the sample. The absorptivity is defined as the ratio of the power per unit area absorbed by the sample, to the power per unit area incident on the sample. This can be written as

$$A = \frac{P_a}{P_o} \quad (60)$$

where P_a is the power absorbed by the sample. Finally, the ratio of the power per unit area transmitted through the sample to the power per unit area incident on the sample is the transmission. In equation form it is

$$T = \frac{P_t}{P_o} . \quad (61)$$

where P_t is the power transmitted through the sample. It should be noted that all three of the above quantities, R , A and T will be functions of the angle of incidence, the wavelength and the polarization of the incident beam. Measurements of R , A and T are made by shining a beam of light on a uniform sample. The sample must be larger than the beam size in order to collect all of the incident radiation. Two quantities must be measured. It is necessary to know the intensity of the incident radiation as well as one of the following, the reflected intensity, in order to compute the reflectivity, the amount of power absorbed in order to compute the absorptivity, or the intensity of the transmitted signal, in order to compute the transmission.

For opaque samples, the transmission, T is zero. In such a case the following relations hold.

$$R = 1 - A \quad (62)$$

or

$$\frac{R}{A} = \frac{1}{A} - 1 \quad (63)$$

which can be written as

$$\frac{P_r}{P_a} = \frac{1}{A} - 1 \quad (64)$$

solving for A from this last relation we have

$$A = \frac{1}{1 + \frac{P_r}{P_a}} \quad (65)$$

Thus it is not always necessary to measure the incident power. This technique will be referred to later.

Many different ways have been used to make these measurements. Usually experimental factors and convenience dictate which is best for any given wavelength region and or type of sample. In this study of cadmium, three different methods of measurement were used. They were as follows: 1) In the wavelength range from $7\text{ }\mu\text{m}$ to $0.4500\text{ }\mu\text{m}$, measurements of A were made at 4.2°K using an optical calorimeter. 2) In the wavelength range from $2\text{ }\mu\text{m}$ to $0.21\text{ }\mu\text{m}$ measurements of R were made at 4.2°K , 77°K and room temperature using a Cary 14 spectrophotometer and a reflectometer described by Hartman and Logothetis (28). 3) In the wavelength range from $3000\text{ }\text{\AA}$ to $600\text{ }\text{\AA}$, measurements of R were made at room temperature using the experimental system described below.

Experimental System for the Vacuum Ultraviolet Spectrum

The experimental setup for making reflectivity measurements in the vacuum ultraviolet is shown schematically in Figure 2. Also a block diagram of the light path and vacuum system is shown in Figure 3.

The system consists of three basic items, a light source emitting a spectrum of radiation, a monochromator used to select a narrow wavelength range of this broad spectrum and reflectometer. The most unique feature of this part of the experiment was the light source. The source was synchrotron radiation from an electron storage ring, specifically, the electron storage ring located in Stoughton, Wisconsin, operated by the Physical Sciences Laboratory of the University of Wisconsin at Madison. The storage ring consisted of a torus-shaped tube into which electrons were injected from a fixed field-alternating gradient accel-

Figure 2. Schematic layout of experimental equipment for the vacuum ultraviolet spectrum

Figure 3. Block diagram of the vacuum system and optical apparatus for the vacuum ultraviolet spectrum

erator. Magnets surrounding the tube guide the electrons in nearly circular orbits, while an r.f. cavity surrounding a section of the tube supplies energy to the electrons in order to compensate for that lost through synchrotron radiation. The radiation is due to the radial acceleration of the electrons. The energy of the electrons can be varied up to 250 MeV. For all the measurements made in this work the storage ring was operated at 240 MeV. At this energy the electrons are highly relativistic, moving with a speed approximately equal to the speed of light. For such a case the radiation is tangent to the electron orbit.

The calculated spectrum of the radiation for several electron energies is shown in Figure 4 and the polarization distribution as a function of angle above and below the plane of the electron orbit is shown in Figure 5. An excellent discussion of synchrotron radiation is given by Jackson (29) in which these quantities are derived. Reviews of the use of synchrotron radiation as a light source in the far ultraviolet are given by Godwin (30), Madden et al. (31) and by Haensel and Kunz (32). In this work the essential features of synchrotron radiation are its spectrum over the wavelength range from 3000 Å to 600 Å and its polarization properties. Also important here is the fact that the intensity of the light is a function of the electron current in the storage ring. Because of scattering by gas molecules, electrons were continually being lost from the beam. This caused the light intensity to decay in essentially an exponential manner. The time constant for this decay was about 30 minutes. This, however, was dependent on the vacuum in the storage ring and on the electron beam intensity.

Figure 4. Wavelength distribution of photon flux through an aperture 6 mm high by 2 mm wide at a distance of 89 cm from the electron orbit, with an electron current of 1.1 mA, for three different electron energies

Figure 3. Photon flux (arbitrary units) versus angle above electron orbit (milliradians) for 2000 angstrom synchrotron radiation from 250 MeV electrons

The synchrotron radiation from the storage ring was focused on the entrance slit of the monochromator by an ellipsoidal mirror. The reflection from the mirror unfortunately reduced the polarization qualities of the light. The monochromator was a McPherson model 225, a one-meter near-normal incidence vacuum monochromator with a Bausch and Lomb concave grating. The grating was ruled with 1200 lines/mm, had a blaze wavelength of 1200 Å, and was coated with aluminum and overcoated with MgF_2 .

From the monochromator the light passed out of the exit slit and to the sample chamber. The sample chamber is shown schematically in Figure 6. Before reaching the sample the light beam encountered successively a filter, a chopper, a beam splitter, and an aperture to limit the beam size. After passing through the aperture the light in one case struck the sample at an angle θ and part was reflected to a 1P28 photomultiplier. In the other case, the sample was removed from the light beam and the 1P28 was moved into a position to measure the direct beam. This permitted the incident and reflected signals to be measured providing the necessary information to determine the reflectivity. The photomultiplier was coated with sodium salicylate (33) in order to convert the short wavelength radiation to longer wavelength light that was detectable by the photomultiplier. As was noted earlier the light beam intensity was not constant in time. Thus it was necessary to measure both the incident radiation and the reflected radiation at nearly the same time or provide a means of correlating two signals at different times. The latter of these two methods was used. This is the function

Figure 6. Schematic diagram of the sample chamber used for the vacuum ultraviolet spectrum

of the beam splitter. The beam splitter is a stainless steel plate coated with sodium salicylate with a 1/4 inch hole in it in order to pass the main portion of the light beam on to the sample. The plate was set at an angle to the incident light beam so that light from the fluorescing sodium salicylate could be viewed perpendicularly to the incident beam. This light was detected by an EMI 6256S photomultiplier and the signal recorded. This signal was used as a reference signal to normalize signals taken at different times.

The electronics associated with the system is shown in Figure 7. The system consists of two similar channels. One channel is for the signals associated with the sample and the other is for the normalizing reference signals. To provide a time varying signal to the synchronous amplifier the light beam was chopped mechanically. This was done with an electrically driven tuning fork at a frequency of 201.5 Hz. The chopper also provided an electrical reference signal of 201.5 Hz for the synchronous amplifiers. Gain was changed by changing load resistors on the photomultipliers. Changing the gain in this manner seemed to give much less base line shift than if the gain of the synchronous amplifiers was changed. Finally the signals from the two synchronous amplifiers were recorded on a two-channel strip chart recorder. The information from the strip charts was later transferred to computer cards and analyzed.

To make a reflectivity measurement the following signals were recorded. First the sample was removed from the light beam and the IP28 was adjusted to receive the incident light beam. The wavelength range

Figure 7. Block diagram of the electronic equipment used for the vacuum ultraviolet spectrum

from 600 Å to 3000 Å was then scanned and the two signals recorded. Next the sample was placed in the beam making an angle θ between the normal to the sample surface and the incident light beam. The 1P28 detector was set at an angle 2θ in order to receive the reflected radiation from the sample. Again the spectrum between 600 Å and 3000 Å was scanned and the signals recorded. This process was repeated for the angle θ equal to $\pm 15^\circ$, $\pm 45^\circ$, $\pm 65^\circ$, and $\pm 70^\circ$. This whole sequence of measurements was carried out for four different orientations of the cadmium sample with respect to the polarization of the light beam. All of the above measurements were made using an entrance and exit slit width of 400 μm . This corresponded to a band pass of less than 7 Å. The time constant used in the synchronous amplifiers was 3 seconds. A scan rate of 1.66 Å per second was used.

Two other types of measurements were also made. In one case polarizers were inserted in the beam and measurements made in order to determine the exact polarization of the light. Three sets of measurements were required using two polarizers. One with both the polarizers horizontal, one with both polarizers vertical and one with the polarizers crossed. This last measurement was used to determine the efficiency of the polarizers.

Each polarizer consisted of four gold mirrors arranged to have a common plane of reflection and so that the light beam made a 60° angle of incidence with each mirror. The polarization was derived from the four successive reflections at or near the pseudo-Brester angle. A discussion of this type of polarizer and its use is given by Rosenbaum

et al. (34) and a similar one is described by Hamm et al. (35).

The second type of measurement was made in order to determine the amount of scattered light in the monochromated beam. It consisted of making a scan through the wavelength range with filters in the beam. Only one filter was found to be of use, LiF. It had a cut-off wavelength of approximately 1050 Å. With no scattered light there should have been no signal at wavelengths shorter than the cut-off. This unfortunately was not the case.

Experimental System for the Visible and Infrared Spectrum

As was noted earlier, it is possible to measure the absorptivity of an opaque sample by measuring the power absorbed by the sample and the power reflected from the sample. The absorptivity was then

$$A = \frac{1}{1 + P_r/P_a} \quad (66)$$

To make such a measurement, a calorimetric technique was used. Light from a monochromator, incident on the sample, was partly absorbed by the sample and partly reflected then absorbed by a gold black absorber. The energy absorbed by the sample and by the gold black absorber caused their temperatures to rise. These temperature increases were detected by changes in resistance in two sensing resistors, one thermally attached to the sample and the other in thermal contact with the gold black absorber. After the sample and absorber had reached the new equilibrium value the changes in temperature for both were recorded and the radiation

was shut off. Then these changes in temperature in the sample and the absorber were duplicated by electrical means. The electrical power needed to cause the same rise in temperature was then measured, and used in Equation 66 to find the absorptivity.

The apparatus used to make such measurements is shown in Figures 8 and 9. The method was first introduced by Pippard (36) to make absorptivity measurements at microwave frequencies. Later, Biondi (23,25,37) used the technique for measurements at microwave and infrared frequencies. Bos (38) has also used this method quite successfully to make measurements over the wavelength range from 10 μm to 0.25 μm . Bos discusses both the advantages and some disadvantages of the system. He mentions that even though the method provides a means of measuring the absolute absorptivity, it has the disadvantages of needing relatively large amounts of light power and the measurements must be made at liquid helium temperature in order to make the heat capacities of the sample and absorber small.

The monochromator used was a Leiss double monochromator. It used prisms for dispersing elements. The various prisms and light source combinations used for the different wavelength ranges are shown in Table 1. All of the measurements made used polarized radiation. The light was polarized by using a silver chloride pile-of-plates or a Glan-prism. The silver chloride pile-of-plates was used whenever the globar light source was used. The Glan-prism was used at all other times. The Glan-prism was mounted at the exit slit of the monochromator while the silver chloride polarizer was mounted at the entrance slit.

Figure 8. Light path and dewar system for the visible and infrared spectrum

Figure 9. Sample chamber and light path for the visible and infrared spectrum

Table 1. Prisms and radiation sources for Leiss monochromator

Wavelength range (microns)	Prism material	Radiation source
0.24 - 0.50	quartz	high pressure mercury arc (1000 watts)
0.50 - 2.0	quartz	tungsten bulb (1000 watts)
2.0 - 6.0	calcium fluoride	globalar (80 watts)
6.0 - 7.0	sodium chloride	globalar (80 watts)

The monochromator inherently polarized the light about 55% with the $\vec{E}$ vector of the light perpendicular to the exit slit. This fact made it more difficult to make measurements of the opposite polarization since it greatly diminished the light intensity.

The circuitry used to supply electrical power to the sample and absorber, and to measure the temperature changes is shown in Figure 10. The absorptivity measurements were made at an angle of 15° . As shown in Appendix A, corrections for both S and P-polarization are needed to get normal incidence reflectivity. The corrections involve the dielectric constants of the material and so in general are hard to make. Here the data were first treated as if they were normal incidence data and the dielectric constants were calculated. Then these dielectric constants were used in the correction factor and the data were corrected to normal incidence. The dielectric constants were again calculated. It was found

Figure 10. Circuitry for supplying and measuring the dc power and for measuring the thermometer resistance

that these corrections changed the measured absorptivities by less than 1.0%.

Figure 11 shows the change in the thermometer resistance as a function of absorbed power on the sample. For an absorbed power of $1 \mu\text{W}$ the temperature of the sample changed about 0.007°K . This caused a corresponding change of resistance of 0.7 ohms out of a total of 350 ohms. To prevent Joule heating a maximum current of $70 \mu\text{A}$ was allowed to flow through the carbon resistor. Thus the change in voltage across the resistor was $50 \mu\text{V}$. This voltage could probably be reproduced to within $1 \mu\text{V}$, the limiting factor being the temperature stability of the apparatus inside the sample chamber. So under these conditions the accuracy of the measurement was about $\pm 2\%$, assuming no error in the measurement of the absorber power. At the long wavelength end of the spectrum, very little light was available and so the accuracy of these measurements suffered. In the wavelength range from 6.5 to 7.0 microns, voltage changes of about $20 \mu\text{V}$ were measured. This corresponded to an accuracy of about $\pm 5\%$. This means that the absorptivity at say 7.0 microns was 0.005 ± 0.0003 neglecting other sources of error.

Sample preparation

All samples were cut from a single crystal ingot of zone refined cadmium. The ingot was purchased from Cominco American Inc., Spokane, Washington. The ingot had a stated purity of 99.9999%.

To prepare a sample the single crystal was first mounted on a goniometer and oriented so that the basal plane of the crystal was vertical and the c-axis of the crystal parallel to the base of the

Figure 11. Change in thermometer resistance as a function of absorbed power on the sample

goniometer. This was done by using the back-reflection Laue x-ray diffraction method. The goniometer and sample were then transferred to a spark-cutter and several cuts about $3/32$ inch apart were made perpendicular to the basal plane. These thin slabs were then cut into rectangles of $1/2$ inch by $3/8$ inch. The rectangles were cut so that the c-axis of the crystal was parallel to the $1/2$ inch side of the rectangle and in the plane of the samples. The accuracy of the alignment was $\pm 2^\circ$. After aligning and cutting, the samples were chemically etched and then mechanically polished. The polishing was done using 4/0 emery paper followed by 1 micron and 0.3 micron aluminum oxide abrasive. The samples were then washed in distilled water and etched. The etch solution consisted of 66.7 grams of CrO_3 and 5 grams of Na_2SO_4 dissolved in 333 milliliters of distilled water. Best results were obtained by holding the samples vertical in the solution, and by cycling the sample between the etch and running distilled water. Typical cycle times were about thirty seconds. The cycle was repeated until the surface was smooth and shining. This usually took about four or five cycles. After etching the sample, it was washed in running distilled water for about five minutes and then in hot ethanol for several minutes. It was then dried in a stream of dry nitrogen and then placed directly in the measuring apparatus.

RESULTS

Absorptivity Measurements

The data taken at 4.2°K between the photon energies of 0.15 eV and 4.5 eV are shown in Figures 12 and 13. The data are also tabulated in Appendix B. Both polarizations are shown. For the case of the electric vector parallel to the optic axis (c-axis) there is a strong absorption peak at 1.10 eV. For the other case, i.e., for the electric vector perpendicular to the optic axis, there is also one strong absorption peak, at 0.98 eV. The latter peak rises sharply on the low energy side but falls slowly forming a plateau region on the high energy side of the peak. For this polarization there is also evidence of a shoulder in the absorption curve at 0.29 eV. The shoulder does not appear in the other polarization; however, in this region of the spectrum the light source is fading out and measurements are difficult to make, so it is possible that a very weak peak may have been missed. The shoulder at 0.29 eV for the case of the electric field perpendicular to the c-axis was confirmed by making measurements on the basal plane of a sample. Because of the near normal angle of incidence this case gave $c \perp \vec{E}$ without using polarized light. The fact that the polarizers were not used, greatly increased the incident light intensity. In both polarizations the absorptivity is tending toward a constant value at the low energy end of the spectrum.

Figure 12. Absorptivity of cadmium in the visible and infrared spectrum. The band-pass of the monochromator in the region of the two peaks was 0.03 eV

Figure 13. Absorptivity of cadmium in the infrared spectrum

Visible Reflectivity Data

Figure 14 shows the reflectivity data taken using a Cary 14 spectrophotometer and a reflectometer described by Hartman and Logothetis (28). Here again data were taken with the c-axis of the crystal both parallel and perpendicular to the electric vector of the light. The measurements were made at room temperature. The same structure is seen in these curves, except here the reflectivity minima are not quite as sharp as they were at 4.2°K .

Reflectivity Data between Photon Energies of 6 eV and 20 eV

The high photon energy reflectivity data are shown in Figure 15. These data have been corrected for scattered light and normalized so that they form a continuous curve with the data taken on the Cary 14. Appendix C describes the method used to make these corrections. The corrections necessary to remove the scattered light were quite severe. Many times corrections of several hundred percent were required. Corrections were greatest in the high energy region of the spectrum. Because of these experimental difficulties, the high energy data were not analyzed further.

Kramers-Kronig Analysis

The data were analyzed using a dispersion integral, often called a Kramers-Kronig (KK) integral. The dispersion integral is used to relate the real and the imaginary parts of the Fourier transform of the Green's function for a system. The system must be linear, time independent

Figure 14. Reflectivity of cadmium at 300°K

Figure 15. Reflectivity of cadmium in the vacuum ultraviolet spectrum.

and causal in order that such a relationship exists. Here we are interested in relating the incident electric field of the light beam, E_{inc} , to the reflected electric field of the light beam, E_{ref} , i.e.

$$E_{inc} = r E_{ref} \quad (67)$$

where r is the Fourier transform of the Green's function, and is related to the properties of the material upon which the light is incident. It should also be noted that the square of the magnitude of r is the reflectivity, R . This system is linear, time independent and causal. Thus there exists a relationship between the real and imaginary parts of r . If r is written as

$$r = |r| e^{i\alpha} \quad (68)$$

and the log is taken, then

$$\ln r = \ln |r| + i\alpha \quad (69)$$

where α is a real angle, called the phase angle. In the above equation the real and imaginary parts are separated; i.e., the $\ln |r|$ is real and $i\alpha$ is imaginary. It is not obvious that a dispersion relation should relate the real and imaginary parts of the $\ln r$, but in fact one does exist and the relation is

$$\alpha(\omega_0) = \frac{2\omega_0}{\pi} P \int_0^\infty \frac{\ln |r|}{\omega_0^2 - \omega^2} d\omega \quad (70)$$

This is shown by Toll (39).

In order to calculate the phase, in principle it is necessary to

know $|r|$ over the complete spectrum from zero to infinity. In practice, however, the largest contribution to the integral arises in the region near ω_0 . For frequencies beyond those measured, an extrapolation procedure can often be used. Here the reflectivity was measured to a photon energy of 20 eV. Beyond 20 eV the reflectivity was assumed to drop linearly up to 100 eV at which point the integral was terminated.

The extrapolation was varied in order to determine its effect on the integral. It was found that the extrapolation had a rather large effect on the value of the integral. Thus such an extrapolation method should not be trusted to give absolute values. It is interesting to note that $\alpha(\omega_0)$ can be written in the following way by doing a partial integration; i.e.,

$$\begin{aligned} \alpha(\omega_0) = & \frac{2\omega_0}{\pi} \left\{ \lim_{\beta \rightarrow 0} \left[\frac{\ln|r|}{\omega_0} \ln \left| \frac{\omega_0 + \omega}{\omega_0 - \omega} \right| \right] \right|_{\omega - \beta}^{\omega + \beta} \\ & + \frac{\ln|r|}{2\omega_0} \ln \left| \frac{\omega_0 + \omega}{\omega_0 - \omega} \right| \right|_{\omega + \beta}^{\infty} \Big] \\ & - \frac{1}{2\omega_0} P \int_0^{\infty} \ln \left| \frac{\omega_0 + \omega}{\omega_0 - \omega} \right| \left[\frac{1}{|r|} \frac{d|r|}{d\omega} d\omega \right] \Big\} . \end{aligned} \quad (71)$$

In this form it can be seen that among other things the value of the integral is dependent upon the derivative of $|r|$ with respect to ω . If $|r|$ is replaced by $\sqrt{R}$, $\alpha(\omega_0)$ can be written as

$$\alpha(\omega_0) = \frac{-1}{2\pi} \int_0^{\infty} \ln \left| \frac{\omega_0 + \omega}{\omega_0 - \omega} \right| \left[\frac{1}{R} \frac{dR}{d\omega} d\omega \right] . \quad (72)$$

This is somewhat revealing since R is actually measured and so the

quantity $\frac{1}{R} \frac{dR}{d\omega}$ can be easily visualized.

Once the phase has been found the complex dielectric function can be obtained from the relations (1)

$$N = \frac{1 - R}{1 + R - 2\sqrt{R} \cos \alpha} \quad (73)$$

$$K = \frac{2\sqrt{R} \sin \alpha}{1 + R - 2\sqrt{R} \cos \alpha} \quad (74)$$

$$\epsilon_1 = N^2 - K^2 \quad (75)$$

$$\epsilon_2 = 2NK \quad (76)$$

It is interesting to note that even though the extrapolation procedure needed to find $\alpha(\omega_0)$ had rather large effects on the value of $\alpha(\omega_0)$ it did not affect the above optical constants very much, particularly in the energy range from 0.15 eV to about 4 eV. In any event the net effect of different extrapolations was to shift the curves of the optical constants up or down and to have very little effect on the shape of the curves. It is also interesting that an error in the reflectivity consisting of a constant multiplied by R gives no error in the optical constants. This can be seen from Equation 27. Also the effect of a constant additive error in R on the dielectric constants has been calculated by P.O. Nilsson and L. Munkby (40). They show that the error in the optical constants is approximately proportional to the error in the reflectivity.

Corrections for Oxide Layer on Sample Surface

Since the samples were exposed to air before the reflectivity and/or absorptivity was measured, an oxide layer developed on the

surfaces (41). This oxide layer affected the results of the measurements. However, by making certain assumptions about the thickness of the oxide layer and by knowing the optical constants for cadmium oxide, it was possible to correct the optical constants for cadmium. The procedure for making these corrections is shown in Appendix D. The corrections did not change the general shape of the curves of the optical constants, however, the magnitudes of the optical constants were changed by about 25%. Also the main peak in the curves for ϵ_2/λ was shifted to a higher photon energy. The shift was about a 4% change.

Figures 16 - 20 show the results of the calculations for ϵ_1 and ϵ_2 for the two polarization cases. These curves were computed from the data before corrections were made to eliminate the effect of the CdO layer. Figures 21 - 26 show the corrected results for ϵ_1 , ϵ_2 , and ϵ_2/λ . Figures 27 and 28 show a comparison between the data of R.H.W. Graves and A.P. Lenham (42) and the present results. In order to compare like data, the room temperature data not corrected for the CdO layer are compared here. The general shape of the curves seems to be in good agreement, however, the magnitudes of the two sets of data are somewhat different. This difference in magnitude is believed to be a result of better sample surfaces used here.

Resistivity Ratio Measurements

The resistivity ratio, the ratio of the resistivity of a material at room temperature to its resistivity at liquid helium temperature, was measured for cadmium. The measurements were made by passing a constant

Figure 16. Real part of the parallel dielectric constant as obtained from a Kramers-Kronig analysis of the absorptivity data

Figure 17: Real part of the perpendicular dielectric constant as obtained from a Kramers-Kronig analysis of the absorptivity data

Figure 18. Imaginary part of both the parallel and perpendicular dielectric constants as obtained from a Kramers-Kronig analysis of the absorptivity data

Figure 19. Comparison of the imaginary part of the parallel dielectric constant at $T = 300^\circ\text{K}$ and $T = 4.2^\circ\text{K}$

Figure 20. Comparison of the imaginary part of the perpendicular dielectric constant at $T = 300^\circ\text{K}$ and $T = 4.2^\circ\text{K}$

Figure 21. Real part of the parallel dielectric constant as obtained from a Kramers-Kronig analysis of the absorptivity data corrected for CdO layer

Figure 22. Real part of the perpendicular dielectric constant as obtained from a Kramers-Kronig analysis of the absorptivity data corrected for CdO layer

Figure 23. Imaginary part of the parallel dielectric constant as obtained from a Kramers-Kronig analysis of the absorptivity data corrected for CdO layer

Figure 24. Imaginary part of the perpendicular dielectric constant as obtained from a Kramers-Kronig analysis of the absorptivity data corrected for CdO layer

Figure 25. The parallel optical conductivity as obtained from a Kramers-Kronig analysis of the absorptivity data corrected for CdO layer

Figure 26. The perpendicular optical conductivity as obtained from a Kramers-Kronig analysis of the absorptivity data corrected for CdO layer

Figure 27. Comparison of the parallel optical conductivity of Graves and Lenham (42) with the present data.

Figure 28. Comparison of the perpendicular optical conductivity of Graves and Lenham (42) with the present data

current through the sample and measuring the voltage drop across the sample; i.e.,

$$\frac{\rho_{300}}{\rho_{4.2}} = \frac{V_{300}/I_{300}}{V_{4.2}/I_{4.2}} = \frac{V_{300}}{V_{4.2}} \quad (77)$$

where ρ_{300} is the resistivity of the material at room temperature and $\rho_{4.2}$ at liquid helium temperature; V_{300} and $V_{4.2}$ are the voltage drops across the sample at room temperature and liquid helium temperature, respectively; I_{300} and $I_{4.2}$ are the currents through the sample and are held constant at one value throughout the measurement.

Two sets of measurements were made, one with the current density parallel to the c-axis of the crystal and the other with the current density perpendicular to the c-axis of the crystal. This permitted both the parallel resistivity ratio, $(\rho_{300}/\rho_{4.2})_{||}$, and the perpendicular resistivity ratio, $(\rho_{300}/\rho_{4.2})_{\perp}$, to be determined. The measured values of these two numbers were

$$(\rho_{300}/\rho_{4.2})_{||} = 15.0 \times 10^3 \quad (78)$$

and

$$(\rho_{300}/\rho_{4.2})_{\perp} = 11.6 \times 10^3 \quad (79)$$

The ratio of the perpendicular resistivity to the parallel resistivity at both 300°K and 4.2°K was also determined. These two values were

$$\frac{\rho_{300 \perp}}{\rho_{300 ||}} = 0.90 \quad (80)$$

and

$$\frac{\rho_{4.2 \perp}}{\rho_{4.2 ||}} = 1.17 \quad (81)$$

DISCUSSION

High Energy Data

As mentioned previously the data in the energy range between 6 eV and 20 eV were subject to certain experimental difficulties. One of these difficulties was the amount of scattered light reaching the detector. It was quite large relative to the "true" signal. The scattered light came mainly from imperfections in the grating. The spectral content of the scattered light was not known; however, because the sensitivity of the detector was much greater at the low energy end of the range, it was the scattered light in this region that caused most of the difficulty. There are several possible partial remedies for the problem of scattered light. One possibility is to try several different gratings choosing the one with the least amount of scattered light. This is not always practical since for economic reasons one is usually limited to one or two gratings. Also, even the best grating will introduce some scattered light and there may be a small amount of stray light entering the detector from sources other than the grating. This latter source of stray light can sometimes be eliminated by the use of baffles.

A second element in the system that can be optimized in order to eliminate scattered light is the detector. Here the response of the detector was highly wavelength dependent being about one-hundred times more sensitive to the long wavelength radiation than to the short wavelength radiation. Because the "true" signals in the short wavelength range were quite weak, even a small amount of scattered light in the highly sensitive range of the detector produced a larger response

than the desired signal. Of course a solution to this problem is to use a detector that has a wavelength-independent response. It may also be possible to use several detectors each of which is sensitive to only a portion of the total spectrum to be scanned, thus eliminating all scattered light outside of the band-pass of the detector. It is interesting to note that the reference signal was found to contain very little scattered light. This was attributed to the fact that the response of the detector system in this channel was relatively flat over the total wavelength range scanned.

Filters can also be useful in eliminating scattered light. Samson (43) lists several filters for the vacuum ultraviolet and their possible uses. Also, the use of filters in conjunction with the electronics of the detector system can sometimes be used to eliminate the scattered light. In this case a filter is alternately switched in and out of the light beam, providing an alternating signal to the detector system. The alternating signal consists of the "true" signal plus scattered light when the filter is out of the light beam and of only the scattered light when the filter is in the light beam. Thus by electronically subtracting the signal with the filter in the beam from the signal with filter out of the beam the "true" signal can be obtained.

Since none of the above methods completely eliminates the scattered light it is usually necessary to use some combination of them in order to reduce the scattered light to a tolerable level. Eliminating scattered light is not a trivial matter.

A second difficulty experienced with the data taken in this energy

range was the inability to normalize the data signal with the reference signal. Signals taken at different times with different electron beam currents were to be correlated by the use of the reference signal. However, because of mechanical instabilities in the sample chamber, monochromator, and mirror chamber, the light beam did not always strike the same portion of the detector. Since the detector was not spatially homogeneous this caused variations in the output which were not compensated for by the reference signal. To eliminate the mechanical instabilities in the system, new mounting frames are being built and installed on the mirror chamber, monochromator, and sample chamber. Also variations in the magnetic field at the detector caused variations in the output that were not accounted for by the reference signal. This can be eliminated by shielding the detector from the magnetic field.

Because of the circumstances under which the data were taken there was no time to incorporate any of the above improvements. For this reason the data were corrected to eliminate the scattered light as shown in Appendix C. The normalization problem was overcome by matching the data to the data taken on the Cary 14 where the two sets of data overlapped.

The high energy data show the general form that would be expected of a metal in this energy range. One inconsistency, however, seems to be the location of the plasma frequency. If the plasma frequency is determined by a zero in the real part of the dielectric constant, these data show the plasma frequency to be at 6.5 eV. Other measurements of the plasma frequency of cadmium place it between 7.5 eV and 9.10 eV (44), the

most recent measurement being the value of 8.68 eV. The cause of this discrepancy no doubt lies in the data. The ϵ_1 curve intersects the abscissa of the graph at a very small angle. Thus only slight changes in the data can cause rather large changes in the point of intersection.

Visible and Near Infrared Spectrum

Most of the structure in the reflectivity and absorptivity of cadmium due to interband transitions is in the visible and near infrared portion of the spectrum. This structure in the optical absorption can be correlated with the band structure of cadmium. In order to make such a correlation it is instructive to consider the pseudopotential model for a crystal. In such a model the electron eigenstates are expanded in a set of plane waves which have been made orthogonal to the core states of the material. The orthogonalization of the plane waves to the core states has the effect of a repulsive potential added to the true crystalline potential. The combination of the true crystalline potential and the effective repulsive potential is called the pseudopotential. If the orthogonalized plane wave (OPW) expansion for the electron wave functions is substituted in the single-particle Schrödinger equation and the orthogonalization terms transposed to the left hand side of the equation the result is (45)

$$\left[\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) + \sum_{\alpha} (E_{\vec{k}} - E_{\alpha}) |\alpha\rangle \langle \alpha| \right] \psi_{\vec{k}}(\vec{r}) = \quad (82)$$

$$\left[\frac{\hbar^2}{2m} \nabla^2 + W(\vec{r}, \vec{k}) \right] \psi_{\vec{k}}(\vec{r}) = E_{\vec{k}} \psi_{\vec{k}}(\vec{r}) ,$$

where $V(\vec{r})$ is the ion-core potential and $|\alpha\rangle$ and E_α are the eigenvectors and eigenvalues of the core states, respectively. The function

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{g}} a_{\vec{g}} |\vec{k} - \vec{g}\rangle, \quad (83)$$

where the sum is over reciprocal lattice vectors, is called the pseudopotential wave function. The pseudopotential, $W(\vec{r}, \vec{k})$, can be written as

$$W = V_L + V_N + V_{SO} \quad (84)$$

where V_L , V_N , and V_{SO} are the local potential, the nonlocal potential, and the spin-orbit interaction, respectively. The terms "local" and "nonlocal" refer to the dependence of the potential on the electron wave vector, $\vec{k}$. A nonlocal potential is dependent on $\vec{k}$ while a local potential is not. Often the pseudopotential is approximated by only the local potential, V_L . In such cases it is convenient to express the local potential as a summation over reciprocal lattice vectors, $\vec{g}$; i.e.

$$V_L(\vec{r}) = \sum_{\vec{g}} V_L(\vec{g}) \exp(i\vec{g} \cdot \vec{r}) \quad (85)$$

where $V_L(\vec{g})$ are the Fourier coefficients of the local pseudopotential. The $V_L(\vec{g})$ can be written as the product of a structure factor, $S(\vec{g})$ and a form factor, $F(\vec{g})$ (46), i.e.

$$V_L(\vec{g}) = S(\vec{g}) F(\vec{g}) \quad (86)$$

The structure factor for close-packed hexagonal materials is

$$S(\vec{g}) = \frac{1}{2} [1 + \exp(i\vec{g} \cdot \vec{s})] \quad (87)$$

where

$$\vec{s} = \frac{1}{2} \vec{a}_1 + \frac{2}{3} \vec{a}_2 + \frac{1}{3} \vec{a}_3 \quad (88)$$

and $\bar{a}_1, \bar{a}_2, \bar{a}_3$ are the real space primitive lattice vectors.

Usually only a few of the Fourier coefficients are taken to be nonzero. For cadmium these are typically those corresponding to the Brillouin zone planes $\langle 100 \rangle$, $\langle 002 \rangle$, and $\langle 101 \rangle$. It is on these planes that the Fermi surface contacts the zone boundaries with nonzero structure factors. The values used for the nonzero local pseudopotential coefficients are usually chosen so that band structure calculations based on the local pseudopotential will fit experimental data. Katsuki and Tsuji (47) have used a local pseudopotential model to calculate the band structure and Fermi surface of cadmium. They used three local pseudopotential coefficients as adjustable parameters and determined the coefficients by fitting experimental data on the Fermi surface. The results of their band structure calculation appear in Figure 29. Figure 30 shows the Brillouin zone of cadmium with the important symmetry points marked.

Another method used to determine the Fourier coefficients is based on optical data showing interband transitions (48). It is assumed that the transitions are a result of Bragg reflections at the Brillouin zone boundaries. Near the zone boundaries it is also assumed that the wave function of the electrons can be expressed as a sum of only two terms, i.e. only the first two terms of Equation 83 are used. Under these conditions the difference in energy, ΔE , between the upper and lower bands for vertical transitions near the zone boundaries is (48)

$$\Delta E = 2 V_{\bar{g}} \sqrt{1 + x^2} \quad (89)$$

where $V_{\bar{g}}$ is the Fourier coefficient of the local pseudopotential corresponding to the Brillouin zone boundary being considered and

Figure 29. Band structure of cadmium by Katsuki and Tsuji (47)

$$x = \frac{(\frac{\hbar \bar{g}}{2})^2 - \bar{p} \cdot \bar{g} \frac{\hbar}{2}}{m V_{\bar{g}}} \quad (90)$$

where $\bar{g}$ is the reciprocal lattice vector for the Bragg plane being considered, $\bar{p}$ is the momentum of the electron, m is the mass of the free electron and $\hbar$ is Planck's constant divided by 2π . ΔE can be related to structure in the optical conductivity. The real part of the optical conductivity is

$$\sigma_1 = \frac{\omega \epsilon_2}{4\pi} \quad (91)$$

where ω is the angular frequency of the incident radiation causing the electronic transitions from the lower energy band to the upper energy band and ϵ_2 is defined in Equation 44. The relation between the maximum in the optical conductivity and the pseudopotential, $V_{\bar{g}}$, is approximately (48)

$$2|V_{\bar{g}}| = \hbar \omega_{\max} \quad (92)$$

where $\omega_{\max}$ is the angular frequency at which a relative maximum in the optical conductivity occurs.

Using this method and the optical data shown in Figures 25 and 26, values for the local pseudopotential coefficients for the $\langle 100 \rangle$, $\langle 002 \rangle$ and $\langle 101 \rangle$ planes have been calculated. Table 2 shows the values derived here and those calculated or fitted to experimental data by other authors (47,49,50). As can be seen there is very little agreement among the values. This is an indication that the local pseudopotential is not an adequate representation for cadmium. The failure of the local pseudopotential is due to the large contribution to the pseudopotential coming from the d shells of the ion cores. The energy of the 4d core states

lies close to, but below the conduction band and causes overcancellation of the Coulomb potential. The p-like and s-like states on the other hand show good cancellation (49). The overcancellation is probably due to the fact that the d electrons are not localized near the ion cores. This causes the repulsive force to have a larger effective range of interaction with the net result being overcancellation of the Coulomb potential.

Table 2. Comparison of local pseudopotential coefficients, $2|V_g|$, in eV

Brillouin zone plane	Peak position (eV)			
	Harrison ^a (50)	Katsuki and Tsuji ^b (47)	Stark and Falicov ^b (49)	Present ^c
100	0.04	0.14	0.64	0.29
002	0.58	1.36	0.46	1.05
101	0.84	0.68	0.79	1.10

^aCalculated from first principles.

^bAdjusted to fit experimental Fermi surface data.

^cAdjusted to fit optical data.

Because of the failure of the local pseudopotential due to the strong contribution of the d-like interactions, it is necessary to use the complete pseudopotential; i.e., it is necessary to consider nonlocal effects in the pseudopotential. A band structure calculation for cadmium using the complete pseudopotential was carried out by R.W. Stark and L.M. Falicov (49). The results of their calculation is shown in Figure 31.

A physical interpretation of the pseudopotential method can be

gained by considering the process of the formation of the pseudopotential. It would appear that the electrons would experience a space-dependent crystalline potential which was strongly attractive near the ion cores. However, due to the Pauli exclusion principle there is also a strong repulsive potential caused by the bound electrons in the ion cores. This repulsive potential tends to cancel the attractive Coulomb potential of the positive ion cores. In the pseudopotential method the plane wave expansion for the electron wave functions is orthogonalized to the core states. This orthogonalization accounts for the Pauli exclusion principle. Because of the cancellation between the Coulomb potential and the potential due to the Pauli exclusion principle, the conduction electrons experience some average potential that has very little spatial variation. It is for this reason that the conduction electrons can be treated as "nearly free electrons" (51). This essentially is the case of the local pseudopotential when only a few of the Fourier coefficients are considered to be nonzero.

Using the band structure of Stark and Falicov (49), only neglecting spin orbit coupling, R.V. Kasowski (52) has calculated the optical conductivity of cadmium. A comparison of ϵ_2^b based on his calculations and the present data is shown in Figures 32 and 33. Although the agreement is not perfect it is much better than for the case of the local pseudopotential.

It should be noted that the calculated curves of Kasowski (52) are based only on interband absorption. The experimental curves on the other hand are affected not only by interband absorption but also by absorption

Figure 32. Comparison of the imaginary part of the experimental parallel interband dielectric constant with that theoretically derived by Kasowski (52) (histogram)

Figure 33. Comparison of the imaginary part of the experimental perpendicular interband dielectric constant with that theoretically derived by Kasowski (52). (histogram)

due to other scattering mechanisms. In order to separate the interband absorption from other absorption processes in the experimental data it was assumed that all absorption processes were independent of photon energy except the interband absorption processes. The values of the energy-independent absorption for the two polarizations were taken to be the measured absorption values at the long wavelength end of the measured spectrum. This "constant" absorption was subtracted from the measured absorption and the optical conductivity was recalculated. The "corrected" conductivity is in somewhat better agreement with Kasowski's calculated curves than the "uncorrected" data. In the perpendicular polarization case, the widths and the heights of the peaks agree to within 10% although the positions of the peaks differed by about 0.25 eV. The main peak in Kasowski's data is at higher energy. In the parallel polarization case, again the widths of the two peaks agree quite well, the experimental width being about 0.95 eV and the calculated width being about 1.05 eV. The heights of the two peaks do not agree as well as in the perpendicular polarization case. The experimental value is about 75 while Kasowski's value is about 105. However the energy positions of the two peaks are in better agreement than in the perpendicular case. The experimental peak is at 1.37 eV and the calculated one at 1.36 eV.

In light of the discussion in the Introduction about interband singular points due to parallel bands, it would be expected that interband optical-absorption would occur between the nearly parallel portions of bands two and three along the symmetry lines ΓK , ΓM and LH . Because of the symmetry selection rules for the close-packed hexagonal structure

(53,54) direct electronic transitions can occur between bands two and three along ΓK and ΓM , only for light polarized along the c-axis of the crystal ($c \parallel \vec{E}$). Thus along ΓK and ΓM the oscillator strengths for perpendicularly polarized light are zero. Along LH the selection rules allow both polarizations to contribute to the absorption. Because of the above selection rules, the perpendicular polarization spectra can be assumed to arise mainly in the LH region of the Brillouin zone. As can be seen from the band structure in Figure 31 the absorption should start at about 1.08 eV and extend to about 2.04 eV. This compares with the experimental values of 0.85 eV for the start of the absorption peak and 1.8 eV for the end of the peak. Although the calculated energy position of the absorption is not the same as the experimental position, the calculated width of the absorption agrees quite well with the observed width. A second feature of the absorption in the perpendicular polarization case is the evidence of a splitting of the main peak. This is due to the sharp change in slope of the second band near the point L (52). It should also be noted that this second peak is much less intense than the first. This is due to the fact that the oscillator strengths near L are smaller than at other points along the LH symmetry line (52). The energy position of this second peak is about 1.5 eV. The abrupt change in slope of the LH symmetry line occurs at approximately 1.8 eV. The difference between these two values is about the same as the difference between the calculated value and the experimental value of the start of the absorption. In other words there seems to be good agreement between calculated and experimental structure but the calculated structure is about 0.25 eV

higher in energy. This may be due to the fact that the calculated band structure is for a crystal at zero degrees Kelvin. As the temperature is increased the shift in the calculated energies will be to lower energies. This is in a direction to give better agreement with the experimental values but will probably not be enough to account for the observed differences. This shift of the peaks to lower energy with an increase in temperature is due to the lessening of the crystal potential.

A much smaller absorption edge was also observed at 0.29 eV for the perpendicular polarization case. It is not exactly obvious what part of the Brillouin zone is contributing to this absorption but it is believed to be due to transitions near the point K. Also absorption can take place throughout the Brillouin zone and not just along the symmetry lines. The calculated band diagrams only show the position of the bands along symmetry lines and thus do not show critical points or the presence of nearly parallel bands that may exist in other parts of the zone. For this reason the band structure alone is not always adequate for explaining optical data.

The parallel polarization case can be discussed in a manner similar to that above. As mentioned earlier, transitions between bands two and three along ΓK and ΓM are allowed by the selection rules as well as transitions along LH. The band structure shows that there are energy differences along ΓK and ΓM that range from 1.03 eV to 1.49 eV and along LH from 1.03 eV to 2.03 eV. The experimental data show the absorption starting at about 0.9 eV having a fairly sharp change in slope at about 1.37 eV and decreasing to background level at about 1.85 eV. Again the

width of the experimental peak agrees quite well with that predicted from the band structure. The change in slope in the experimental data at 1.37 eV is attributed to the fact that the absorption along ΓK and ΓM drops off at this energy. Here again the energy position of the change in slope is in good relative agreement with the calculated position. For the parallel polarization case the calculated values are shifted to higher energies by approximately 0.13 eV with respect to the experimental data.

Absorption Due to Conduction-Electrons

As can be seen in Figure 13 the low temperature absorptivities for both polarizations appear to become independent of wavelength at the infrared end of the spectrum. This is as expected for the conduction-electron absorption processes discussed in the Introduction. For the parallel polarization case the absorptivity becomes approximately wavelength-independent for energies smaller than about 0.27 eV. The absorptivity at this energy is 0.01. For the perpendicular polarization there is an absorption edge at 0.29 eV as discussed earlier. Because of this interband effect, the absorption becomes wavelength independent only for energies less than 0.20 eV. In this energy range the absorptivity is 0.007. These values of absorptivity can be compared with those predicted from Equations 49 and 57. Equation 49 has been derived for S-polarized light. The γ that appears in the equation is an effective γ , used to account for important damping effects in the crystal. For this analysis γ_{eff} derived from Equation 54 will be used. As mentioned in the Introduction, γ_{eff} is greatly increased by electron-phonon interactions. For

the samples used here γ_{eff} is about 4×10^3 times the value of γ derived from the dc conductivity at 4.2°K . The latter would be based mainly on impurity scattering and would not account for electron-phonon interactions.

In order to calculate the absorptivity it is necessary to know certain physical quantities for cadmium. These have been obtained from the literature or calculated using a free electron model. For cadmium the Debye temperature, $\theta = 209^\circ\text{K}$ has been taken from specific-heat data (55). The conductivity is anisotropic. The values of the conductivity at 273°K used here have been taken from the literature (56) and are $\sigma_{\parallel} = 1.30 \times 10^7/\text{ohm-meter}$ and $\sigma_{\perp} = 1.58 \times 10^7/\text{ohm-meter}$. The conduction-electron density, n , has been calculated from the mass density and has a value of 9.27×10^{22} electrons per cubic centimeter. The effective mass in cadmium is also anisotropic. There is very little information on the anisotropic effective mass of cadmium in the literature. Here the free electron mass, m , has been used. The Fermi velocities have been calculated using a free electron model for the crystal; i.e.

$$v = \frac{\hbar}{m} (3\pi^2 n)^{1/3} \quad (93)$$

where v is the Fermi velocity. The value for both the parallel and the perpendicular velocities is 1.62×10^6 meters per second. Thus all anisotropy in the absorptivity, as calculated here, will come from the anisotropy in conductivity through γ_{eff} .

Using the above values for the parallel polarization case, and Equations 49, 54, 55 and 56, the absorptivity was calculated to be 0.0103 which is in good agreement with the experimental value. If

Equation 57, derived by Holstein (22), is used to calculate the absorptivity, instead of Equation 49, the result is 0.0125. Although the two values are nearly the same the more exact equation of Kliwer and Fuchs (21) gives better agreement with experiment. At the present time there is some doubt as to the meaning of the results, since the effective mass is not known and some of the other quantities may prove to be incorrect. However, it does seem that the theory of Kliwer and Fuchs correctly describes the optical properties of cadmium in the infrared. It should also be noted that the agreement between the theory and experiment further confirms the electron-phonon interaction process proposed by Holstein (26), since it is this interaction that causes the relatively large γ_{eff} .

For the perpendicular polarization case the incident radiation was P-polarized. At the present time there are no theories that treat the P-polarization case exactly. In lieu of a better approach, the same equations as used above are used here, but the angle of incidence, ϕ is taken to be zero instead of 15° as it actually was in the experiment. The calculated absorptivity using the Kliwer-Fuchs (21) theory is 0.0094. This compares with 0.0099 derived from the simpler equation due to Holstein (22). Here the agreement with experiment is not as good as it was for the parallel polarization case. This may be due to the inability of the theory to treat the P-polarized light even though the angle of incidence was small. More likely, however, it is the fact that the mass of the electrons is taken to be the free electron mass and not an effective mass.

It is interesting to calculate effective masses for the electrons in

cadmium by using the experimental data and the theory of Kliever and Fuchs. This is done by finding the masses for which the agreement between the experimental absorptivity and the calculated absorptivity is exact. The calculations were made as above only now the masses were considered to be effective masses. The results for the parallel case and for the perpendicular case are

$$m_{||}^* = 1.09 m \quad (94)$$

and

$$m_{\perp}^* = 1.61 m \quad (95)$$

The thermal effective mass, m_t^* , for cadmium was also calculated using specific-heat data (57) and the following equation (58),

$$m_t^* = \frac{\gamma_C}{\gamma_{CF}} \quad (96)$$

The constant, γ_{CF} is defined by

$$\gamma_{CF} = \frac{\pi^2 k_B^2 N_0}{2E_F} \quad (97)$$

where E_F is the free electron Fermi energy, k_B is Boltzmann's constant and N_0 is Avogadro's number. The constant, γ_C is defined through the heat capacity, C .

$$C = \gamma_C T + AT^3 \quad (98)$$

where T is the temperature and A is a constant. Using the above, the thermal effective mass is found to be

$$m_t^* = 1.45 \quad (99)$$

The weighted average of the effective masses given in Equations 95 and 96 is

$$m_{op}^* = \frac{2m_{\perp}^* + m_{\parallel}^*}{3} = 1.44 m \quad (100)$$

The agreement between m_{op}^* and m_t^* as calculated above is rather good considering the possibility of experimental error and the lack of an exact theory for treating the P-polarized light. This agreement suggests the electrons contributing to long wavelength low-temperature absorption are "free electron like" as assumed.

SUMMARY

The reflectivity and/or absorptivity of cadmium was measured from 0.15 eV to 20 eV. Measurements were made using polarized light with the electric vector of the incident radiation both perpendicular and parallel to the c-axis of the crystal. Unfortunately the data in the range from 6 eV to 20 eV could only be treated qualitatively because of the experimental difficulties.

In the visible and infrared spectra, both polarization cases had strong absorption peaks. In the perpendicular polarization case the main peak was at 0.98 eV and was attributed mainly to transitions between bands two and three along the LH symmetry line. Also in this polarization there was an absorption edge at 0.29 eV. This may be due to transitions near the point K in the Brillouin zone. For the parallel polarization case the main absorption peak was at 1.10 eV. The absorption here was attributed to transitions between bands two and three along ΓK , ΓM and LH. No low energy absorption edge was found for the parallel polarization case. Agreement between the experimental data and theoretical calculations based on a nonlocal pseudopotential model was good. However, there was no agreement between the data and calculations based on a local pseudopotential model.

At low temperatures, the long wavelength absorptivities were approximately constant. This agrees with the theories of Kliwer and Fuchs and of Holstein for the anomalous skin effect region. Using the theory of Kliwer and Fuchs and the experimental data, parallel and perpendicular effective masses were calculated. The values were 1.09 m

and $1.61 m$, respectively. The weighted average of $m_{||}^*$ and $m_{\perp}^*$ is in good agreement with the thermal effective mass for cadmium. The low energy data support the theory of Kliewer and Fuchs and tend to confirm the volume absorption process suggested by Holstein.

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APPENDICES

Appendix A. Correction for a Non-Normal Angle of Incidence

Because of experimental difficulties, reflectivities are not made at exactly normal incidence. However, methods for analyzing the data usually assume normal incidence. This dilemma is overcome by correcting the data to make it equivalent to normal incidence data.

Using classical optics, the corrections that are necessary can be found by considering Equations 101, and 108 for the reflection coefficients. First consider the S-polarization case. Here

$$r_s = \frac{\cos \varphi - \sqrt{\epsilon - \sin^2 \varphi}}{\cos \varphi + \sqrt{\epsilon - \sin^2 \varphi}} \quad (101)$$

where φ is the angle of incidence. For small angles of incidence the following approximations are valid.

$$\cos \varphi = 1 - \varphi^2/2 \quad (102)$$

$$\sin^2 \varphi = \varphi^2 \quad (103)$$

$$\sqrt{\epsilon - \sin^2 \varphi} = \sqrt{\epsilon} \left(1 - \frac{\varphi^2}{2\epsilon}\right) \quad (104)$$

Introducing these approximations into Equation 101 the expression for r_s becomes

$$r_s = \frac{\left(1 - \frac{\varphi^2}{2}\right) - \sqrt{\epsilon} \left(1 - \frac{\varphi^2}{2\epsilon}\right)}{\left(1 - \frac{\varphi^2}{2}\right) + \sqrt{\epsilon} \left(1 - \frac{\varphi^2}{2\epsilon}\right)} \approx r_o \left(1 + \frac{\varphi^2}{\sqrt{\epsilon}}\right) \quad (105)$$

where r_o is the normal incidence amplitude reflection coefficient. Thus

$$R_s \approx R_o \left(1 + \frac{2\varphi^2 N}{N^2 + K^2}\right) \quad (106)$$

where use has been made of the relation

$$\sqrt{\epsilon} = N + iK \quad (107)$$

For the P-polarization case the reflection coefficient is

$$r_p = \frac{\sqrt{\epsilon} - \sin^2 \varphi - \sqrt{\epsilon} \cos \varphi}{\sqrt{\epsilon} - \sin^2 \varphi + \sqrt{\epsilon} \cos \varphi} \quad (108)$$

For small angles this expression can be approximated by

$$r_p = \frac{1 - \sqrt{\epsilon}}{1 + \sqrt{\epsilon}} \frac{1 - \frac{\varphi^2}{2} \left(\frac{\sqrt{\epsilon} + 1/\sqrt{\epsilon}}{1 - \sqrt{\epsilon}} \right)}{1 - \frac{\varphi^2}{2} \left(\frac{1/\sqrt{\epsilon} - \sqrt{\epsilon}}{1 + \sqrt{\epsilon}} \right)} \quad (109)$$

where the same approximation procedure was used here as was used for r_s . From r_p the reflectivity for small angles can be found. It is

$$R_p \approx R_o \left(1 - \frac{\varphi^2 N}{N^2 + K^2} \right) \quad (110)$$

Using the above two equations for R_p and R_s the normal incidence reflectivity, R_o , can be calculated for the two polarization cases. For S-polarization

$$R_o \approx R_s \left(1 - \frac{2\varphi^2 N}{N^2 + K^2} \right) \quad (111)$$

and for P-polarization

$$R_o \approx R_p \left(1 - \frac{2\varphi^2 N}{N^2 + K^2} \right) \quad (112)$$

As can be seen, in order to correct the reflectivity both N and K for the material must be known. In most cases it is N and K that are to be found from the reflectivity data, thus an iteration process must be used. Here N and K are first calculated from the uncorrected data and then used in Equations 111 and 112 to obtain R_o . The optical constants are then computed using R_o . A second correction to R_o made less than 0.1% change.

Appendix B. Tabulation of Absorptivity Data

The absorptivity of cadmium was measured for two polarization cases. In one case the electric vector of the incident radiation was parallel to the c-axis of the crystal ($c \parallel \vec{E}$) and in the other case it was perpendicular to the c-axis of the crystal ($c \perp \vec{E}$). The data were accurately plotted on a large graph. Values obtained from this graph appear in Table 3.

Table 3. Reflectivity measurements of cadmium at 4.2°K

Energy (eV)	c $\perp$ $\vec{E}$	c $\parallel$ $\vec{E}$	Energy (eV)	c $\perp$ $\vec{E}$	c $\parallel$ $\vec{E}$
0.1500	.9932	.9900	0.9500	.4938	.9120
0.1750	.9930	.9900	0.9600	.3700	
0.2000	.9928	.9900	0.9700	.2650	
0.2250	.9926	.9900	0.9750		.8762
0.2500	.9923	.9902	0.9800	.3100	
0.2625	.9922		0.9900	.3512	
0.2688	.9919		1.0000	.3924	.8200
0.2750	.9917	.9905	1.0100	.4338	
0.2813	.9913		1.0200	.4750	
0.2875	.9906		1.0250		.7637
0.2938	.9900		1.0300	.5163	
0.3000	.9896	.9905	1.0400	.5425	
0.3063	.9892		1.0500	.5613	.6963
0.3125	.9888		1.0600	.5785	
0.3188	.9885		1.0700	.5910	
0.3250	.9882	.9905	1.0750		.5875
0.3313	.9879		1.0800	.6020	.5537
0.3375	.9877		1.0900	.6170	.4930
0.3438	.9874		1.1000	.6265	.5125
0.3500	.9872	.9902	1.1200	.6445	.5463
0.3750	.9867	.9895	1.1400	.6588	.5800
0.4000	.9860	.9890	1.1600	.6738	.6040
0.4250	.9852	.9888	1.1800	.6870	
0.4500	.9843	.9888	1.2000	.6995	.6540
0.4750	.9834	.9885	1.2250		.6715
0.5000	.9825	.9885	1.2500	.7215	.6962
0.5250	.9816	.9881	1.2750		.7135
0.5500	.9807	.9875	1.3000	.7360	.7290
0.5750	.9795	.9869	1.3250		.7440
0.6000	.9782	.9861	1.3500	.7450	.7580
0.6250	.9774	.9852	1.3750		.7713
0.6500	.9761	.9840	1.4000	.7525	.7790
0.6750	.9743	.9827	1.4250		.7855
0.7000	.9722	.9812	1.4500	.7560	.7900
0.7250	.9685	.9793	1.4750		.7945
0.7500	.9632	.9773	1.5000	.7580	.8000
0.7750	.9575	.9750	1.5500	.7605	.8085
0.8000	.9503	.9723	1.6000	.7675	.8163
0.8250	.9438	.9688	1.6500	.7745	.8220
0.8500	.9288	.9647	1.7000	.7825	.8275
0.8750	.8950	.9597	1.7500	.7920	.8345
0.9000	.8350	.9530	1.8000	.7988	.8395
0.9250	.6963	.9350	1.8500	.8125	.8455

Table 3. (Continued)

Energy (eV)	$c \perp \bar{E}$	$c \parallel \bar{E}$	Energy (eV)	$c \perp \bar{E}$	$c \parallel \bar{E}$
1.9000	.8260	.8500	3.2500	.8350	.8490
1.9500	.8335	.8540	3.3000	.8335	.8460
2.0000	.8380	.8575	3.3500	.8312	.8415
2.0500	.8410	.8620	3.4000	.8285	.8370
2.1000	.8425	.8650	3.4500	.8240	.8325
2.1500	.8462	.8650	3.5000	.8215	.8280
2.2000	.8465	.8615	3.5500	.8200	.8237
2.2500		.8585	3.6000	.8195	.8210
2.3000	.8490	.8575	3.6500	.8165	.8163
2.3500		.8565	3.7000	.8160	.8125
2.4000	.8490	.8550	3.7500	.8140	.8097
2.4500		.8555	3.8000	.8115	.8015
2.5000	.8490	.8565	3.8500	.9060	.7990
2.5500		.8575	3.9000	.7975	.7970
2.6000	.8480	.8580	3.9500	.7945	.7945
2.6500		.8600	4.0000	.7915	.7915
2.7000	.8470	.8610	4.0500	.7830	.7830
2.7500		.8610	4.1000	.7735	.7735
2.8000	.8460	.8610	4.1500	.7630	.7630
2.8500		.8600	4.2000	.7515	.7515
2.9000	.8455	.8590	4.2500	.7380	.7380
2.9500		.8575	4.3000	.7245	.7245
3.0000	.8450	.8555	4.3500	.7080	.7080
3.0500	.8435	.8537	4.4000	.6910	.6910
3.1000	.8420	.8537	4.4500	.6720	.6720
3.1500	.8390	.8537	4.5000	.6435	.6435
3.2000	.8380	.8518			

Appendix C. Scattered Light Corrections

The data taken in the wavelength range between 3000 Å and 600 Å had a large amount of scattered light mixed with the "true" signals. In fact the intensity of the scattered light was much larger than that of the "true" signals. The scattered light was mainly due to imperfections in the grating. In the experiment it is very difficult to eliminate the scattered light, so it must be corrected for analytically. This is done by assuming that the measured signals are composed of the sum of the "true" signals and the scattered light. Thus the following relations can be written

$$I_m(\lambda) = I(\lambda) + S(\lambda) \quad (113)$$

and

$$I_{om}(\lambda) = I_o(\lambda) + S_o(\lambda) \quad (114)$$

where I_m is the measured signal reflected from the sample, I is the "true" reflected signal, S is the scattered light reflected from the sample, I_{om} is the direct beam intensity, I_o is the "true" beam intensity, S_o is the scattered light in the direct beam and λ is the wavelength of the radiation. All of the above quantities have been normalized to account for differences in the electron beam current in the storage ring and the different amplifier gain settings used. Using Equations 113 and 114 the reflectivity, R , can be written as

$$R(\lambda) = \frac{I(\lambda)}{I_o(\lambda)} = \frac{I_m(\lambda) - S(\lambda)}{I_{om}(\lambda) - S_o(\lambda)} \quad (115)$$

It is now necessary to determine the functions $S(\lambda)$ and $S_o(\lambda)$. In general

they can be written as

$$S(\lambda) = \int_0^{\infty} F(\lambda, \lambda') R(\lambda') d\lambda' \quad (116)$$

and

$$S_0(\lambda) = \int_0^{\infty} F(\lambda, \lambda') d\lambda' \quad (117)$$

where the function $F(\lambda, \lambda')$ is the response function for the signal channel. It includes the detector response and monochromator characteristics. It is assumed that the function $F(\lambda, \lambda')$ can be written as

$$F(\lambda, \lambda') = g(\lambda) h(\lambda') \quad (118)$$

This assumption appears to be compatible with the experimental data. This allows S and S_0 to be written in the following way

$$S(\lambda) = g(\lambda) \int_0^{\infty} h(\lambda') R(\lambda') d\lambda' = g(\lambda) K \quad (119)$$

and

$$S_0(\lambda) = g(\lambda) \int_0^{\infty} h(\lambda') d\lambda' = g(\lambda) K_0 \quad (120)$$

where K and K_0 are constants which can be evaluated from experimental measurements.

The function $g(\lambda)$ and the constants K and K_0 were determined by making measurements using a LiF filter which had a cutoff wavelength of 1050 Å. Signals detected at wavelengths shorter than the cutoff wavelength were due to scattered light. It was found that the scattered light intensity followed an exponential curve and could be written as

$$g(\lambda) = 1.0 + 7.9 e^{-2.2 \times 10^{-3} \lambda (\text{Å})} \quad (121)$$

Once the function $g(\lambda)$ was determined it was only necessary to find the constants K and K_0 . This was done by measuring the scattered light

intensity at a wavelength shorter than 1050 Å using the LiF filter for each wavelength scan. Thus

$$R(\lambda) = \frac{I_m - K g(\lambda)}{I_{om} - K_o g(\lambda)} \quad (122)$$

where all of the quantities on the right side of Equation 122 can be measured.

Appendix D. Correction for CdO Layer on Sample Surface

It is very difficult to prepare a metal sample for optical measurements and not allow the surface to oxidize before the measurements are made. Even if the sample is exposed to air for only a few minutes, a many angstrom thick layer of the metal oxide will form (41). This oxide layer has a greater or lesser effect on the measurements of the optical properties of the metal depending upon the optical properties of the oxide and on the thickness of the oxide layer. The optical constants for the oxide can often be found in the literature or they can be measured. The thickness of the oxide layer on the other hand may be difficult to measure and an estimate of its value may be the best that can be done. However, if one has in hand these two pieces of information then the following method may be used to correct the optical constants of the metal.

The procedure is as follows. First the solution for the amplitude coefficient of reflection at the air-oxide interface is obtained for the case of an oxide layer on a metal surface. This situation is illustrated in Figure 34. The solution is obtained by assuming a solution to Maxwell's equations of the form $\vec{E}(\vec{x}, t) = \vec{E}_0 e^{i(\vec{k} \cdot \vec{x} - \omega t)}$ in each material and forcing these solutions to satisfy the boundary conditions of the problem. Here $\vec{k}$ is the wave vector for the wave and has a magnitude of $N \frac{\omega}{c}$ where ω is the angular frequency of the incident radiation and N is the complex dielectric constant for the material. The boundary conditions are obtained from Maxwell's equations. They are: 1) the normal components of $\vec{B}$ and $\vec{D}$ are continuous and 2) the tangential

Figure 34. Orientation of the incident light beam, metal oxide and metal

components of $\vec{H}$ and $\vec{E}$ are continuous.

Using the assumed solutions for the electric field and the boundary conditions, a solution for the amplitude reflection coefficient can be obtained for both S-polarization and for P-polarization. They are:

$$r_s = \frac{(N_1 \cos \varphi - N_1 N_2) \cos \frac{\omega}{c} d N_1 + i(N_1^2 - N_2 \cos \varphi) \sin \frac{\omega}{c} d N_1}{(N_1 \cos \varphi + N_1 N_2) \cos \frac{\omega}{c} d N_1 - i(N_1^2 + N_2 \cos \varphi) \sin \frac{\omega}{c} d N_1} \quad (123)$$

and

$$r_p = \frac{(N_1 \cos \theta \cos \gamma - N_1 N_2 \cos \theta \cos \varphi) \cos \frac{\omega}{c} d N_1 + i(N_1^2 - N_2 \cos \varphi) \sin \frac{\omega}{c} d N_1}{(N_1 \cos \varphi + N_1 N_2) \cos \frac{\omega}{c} d N_1 - i(N_1^2 + N_2 \cos \varphi) \sin \frac{\omega}{c} d N_1} \quad (124)$$

where N_1 is the complex index of refraction of the oxide layer, N_2 is the complex index of refraction of the metal, d is the thickness of the oxide layer, ω is the angular frequency of the incident radiation, and c is the velocity of light. It is assumed that N_1 is known from some previous measurement. The angles θ and γ are shown in Figure 34. φ is the angle of incidence and can be related to θ and γ in the following way:

$$\cos \theta = \sqrt{1 - \frac{1}{N_1^2} \sin^2 \varphi} \quad (125)$$

and

$$\cos \gamma = \sqrt{1 - \frac{1}{N_2^2} \sin^2 \varphi} \quad (126)$$

If the metal plus oxide layer is now considered as a composite material, a coefficient of reflection can be obtained for it in a manner similar to the above method. The results are

$$r_{sc} = \frac{\cos \varphi - \sqrt{N^2 - \sin^2 \varphi}}{\cos \varphi + \sqrt{N^2 - \sin^2 \varphi}} \quad (127)$$

and

$$r_{pc} = \frac{\sqrt{N^2 - \sin^2 \phi} - N^2 \cos \phi}{\sqrt{N^2 - \sin^2 \phi} + N^2 \cos \phi} \quad (128)$$

where N is the complex dielectric function for the composite material. N can be computed from reflectivity data taken on the sample plus oxide layer. It is assumed that N_1 is known from some previous measurement.

By equating r_s to r_{sc} and r_p to r_{pc} solutions for N_2 for the two polarization cases can be obtained. The optical constants for the metal are then

$$\epsilon_1 = \text{Real part of } N_2^2 \quad (129)$$

and

$$\epsilon_2 = \text{Imaginary part of } N_2^2 \quad (130)$$

For the present work optical constants for CdO were taken from a paper by M. Altwein et al. (59). The thickness of the oxide layer was assumed to be 35 Å.